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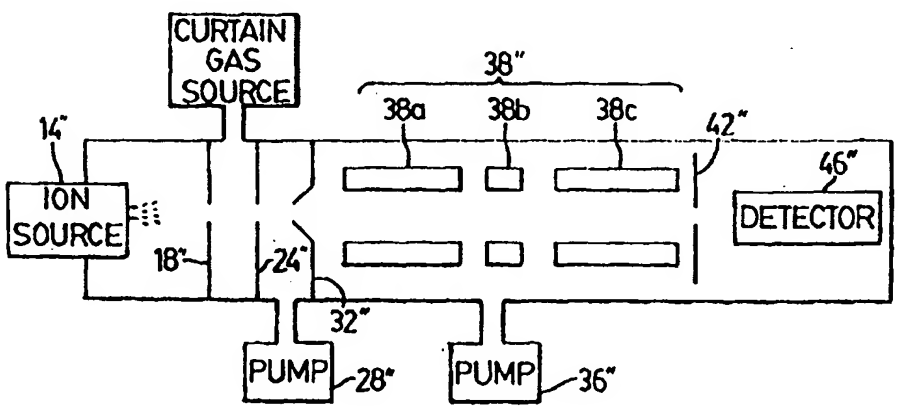


(57) Abstract

A method of operating a mass spectrometer having an elongated multipole rod set, in which a two-dimensional RF field radially contains trapped ions in a mass to charge range of interest, and in which the ions are contained axially by a barrier field on an end lens and to which a low voltage DC is applied. Trapped ions are axially mass selectively ejected by taking advantage of the mixing of the degrees of freedom induced by the fringing fields and other anti-harmonicities in the vicinity of the end lens. Thus, ions can be mass selectively ejected at the exit end at the same time as ions are being admitted into the entrance end of the rod set, thereby taking better advantage of the ion flux from a continuous ion source. The axial mass selective ejection is performed by applying an auxiliary AC voltage to the end lens, and by scanning either the auxiliary AC voltage or the RF voltage on the rod set. Trapped ions can be concentrated near the exit lens by applying an axial field in the direction of the lens, or can be depleted by applying the axial field in the opposite direction. The axial field can be oscillated to dissociate trapped ions.

Title: AXIAL EJECTION IN A MULTIPOLE MASS SPECTROMETER

FIELD OF THE INVENTION

This invention relates to a multipole elongated rod ion trap mass spectrometer with axial ejection.

BACKGROUND OF THE INVENTION

Conventional ion traps, of the kind described in U.S. patent 2,939,952, are generally composed of three electrodes, namely a ring electrode, and a pair of end caps, with appropriate RF and DC voltages applied to these electrodes to establish a three-dimensional field which traps ions within a mass range of interest in the relatively small volume between the ring electrode and the end caps. The electrodes may be hyperbolic, producing a theoretically perfect three-dimensional quadrupole field, or they may deviate from hyperbolic geometry, giving rise to additional multipole fields superimposed on the quadrupole field and which can produce improved results.

Usually ion trap mass spectrometers are filled in an essentially mass-independent manner and are emptied mass-dependently by manipulating the RF and DC voltages applied to one or more of the electrodes. The ion storage and fast scanning capabilities of the ion trap are advantageous in analytical mass spectrometry. High analysis efficiency, compared to typical beam-type mass spectrometers, can be achieved if the time to eject and detect ions from the trap is smaller than the time required to fill a trap. If this condition is met, then very few ions are wasted.

However an inherent disadvantage of ion traps is that ion transport into the trap is usually of very low efficiency, e.g. one to ten percent, primarily due to the relatively small volume of the trap and the very demanding ion energetic constraints for trap acceptance of externally generated ions. The relatively small volume of the ion trap means that the number of ions that can be accepted before space charge effects become

serious is also relatively small. Increasing the radial dimension of the volume of the trapping chamber of a conventional ion trap partially overcomes this limitation, but with the additional disadvantages of reduced analytical utility and/or increased costs (e.g. reduced mass range, larger power supplies). The small volume of the ion trapping chamber will also tend to limit the linear response range (i.e. dynamic range), again because of the effects of space charge at high ion densities.

An additional problem is that when a conventional ion trap is performing an analysis, no additional ions can be accepted. For many modern ion sources such as electrospray, ion spray (disclosed in U.S. patent 4,861,988), or corona discharge, this can be a considerable disadvantage because the trap fill time is usually short compared with the analysis time. Consequently, and as described in U.S. patent 5,179,278 assigned to the assignee of the present invention, many ions can be wasted during the analysis time, resulting in relatively low duty cycles.

It is known that ions can be trapped and stored very efficiently in a two-dimensional RF quadrupole. In some cases ions have been admitted into and then trapped in a two-dimensional quadrupole for purposes of releasing them into a conventional ion trap, as shown in U.S. patent 5,179,278. More generally ions have been admitted into a pressurized linear cell or a two-dimensional RF quadrupole for the purpose of studying ion molecule reactions. Generally the ions enter the device from a mass selective source such as a resolving quadrupole, are trapped for a specified period of time, and then are ejected mass-independently for subsequent mass analysis.

U.S. patent 5,420,425 teaches that ions can be trapped and stored in a two-dimensional RF quadrupole and scanned out mass-dependently, using the technique of mass selective instability. According to that patent the device disclosed therein was conceived in order to improve ion sensitivities, detection limits, and dynamic range, by increasing the volume of the trapping chamber in the axial dimension. The mass selective instability mode of ion ejection (and all other mass

analysis scanning modes described in U.S. patent 5,420,425) involve ejecting ions out of the trapping chamber in a direction orthogonal to the center axis of the device, i.e. radially.

There are several disadvantages of radial ejection of ions from a two-dimensional RF quadrupole. One disadvantage is that radial ejection expels ions through or between the quadrupole (or higher order multipole) rods. This forces the ions through regions of space for which there are significant RF field imperfections. The effect of these imperfections is to eject ions at points not predicted by the normal stability diagram.

Radial ejection from a two-dimensional RF quadrupole has the further disadvantage of providing a poor match between the dimensions of the plug of ejected ions and conventional ion detectors. In a linear or curved rod structure, radially ejected ions will exit throughout the length of the device, i.e. with a rectangular cross-section of length corresponding to the rods themselves. Most conventional ion detectors have relatively small circular acceptance apertures (e.g. less than 2 cm^2) that are not well-suited for elongated ion sources.

Mass selective instability for radial ion ejection of ions from a two-dimensional RF quadrupole has additional problems. Ions ejected radially from such a device will exit with a diverging spatial profile with a characteristic solid angle. Some of the ejected ions will hit the rods and be lost. In addition, radially ejected ions will leave the trapping structure in opposite directions. Multiple ion detectors would be required to collect all of the ions made unstable by this and similar techniques. Ions ejected away from the detector(s) or which encounter one of the electrodes are lost and therefore do not contribute to the measured ion signal. Therefore only a small fraction of trapped ions would normally be collected, despite the very high storage ability of this device.

BRIEF SUMMARY OF THE INVENTION

Accordingly, it is an object of the present invention in one of

its aspects to provide an elongated multipole mass spectrometer which has a high injection efficiency and an enlarged trapping volume, and in which ions are ejected along the major axis of the device, thus allowing a good geometric match with commonly used ion detectors.

In one of its aspects the invention provides a method of operating a mass spectrometer having an elongated rod set, said rod set having an entrance end and an exit end and a longitudinal axis, said method comprising:

(a) admitting ions into said entrance end of said rod set,

(b) trapping at least some of said ions in said rod set by producing a barrier field at an exit lens adjacent to the exit end of said rod set and by producing an RF field between the rods of said rod set adjacent at least the exit end of said rod set,

(c) said RF and barrier fields interacting in an extraction region adjacent to said exit end of said rod set to produce a fringing field,

(d) energizing ions in said extraction region to mass selectively eject at least some ions of a selected mass to charge ratio axially from said rod set past said barrier field,

(e) and detecting at least some of the ejected ions.

Further objects and advantages of the invention will be apparent from the following description, taken together with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

In the drawings:

Fig. 1 is a diagrammatic view of a simple mass spectrometer apparatus with which the present invention may be used;

Fig. 1a is an end view of a rod set of Fig. 1 and showing electrical connections to such rod set;

Fig. 2 is a diagrammatic view of a modification of a part of the apparatus of Fig. 1;

Fig. 3 is a diagrammatic view of a further modification of the apparatus of Fig. 1;

Fig. 4 is a diagrammatic view of another modification of the Fig. 1 apparatus;

Fig. 5 is a graph showing results obtained with the apparatus of Fig. 4;

Fig. 6 is a graph showing further results obtained with the Fig. 4 apparatus;

Fig. 7 is an end view of rods which can be used as an exit lens; and

Fig. 8 is a plan view of a modified exit lens.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENT

Reference is first made to Fig. 1, which shows a mass analyzer system 10 with which the invention may be used. The system 10 includes a sample source 12 (normally a liquid sample source such as a liquid chromatograph) from which sample is supplied to a conventional ion source 14. Ion source 14 may be an electrospray, an ion spray, or a corona discharge device, or any other known ion source. An ion spray device of the kind shown in U.S. patent 4,861,988 issued August 29, 1989 to Cornell Research Foundation Inc. is suitable.

Ions from ion source 14 are directed through an aperture 16 in an aperture plate 18. Plate 18 forms one wall of a gas curtain chamber 19 which is supplied with curtain gas from a curtain gas source 20. The curtain gas can be argon, nitrogen or other inert gas and is described in the above-mentioned U.S. patent 4,861,988. The ions then pass through an orifice 22 in an orifice plate 24 into a first stage vacuum chamber 26 evacuated by a pump 28 to a pressure of about 1 Torr.

The ions then pass through a skimmer orifice 30 in a skimmer plate 32 and into a main vacuum chamber 34 evacuated to a

pressure of about 2 milli-Torr by a pump 36.

The main vacuum chamber 34 contains a set of four linear conventional quadrupole rods 38. The rods 38 may typically have a rod radius r=0.470cm, an inter-rod dimension r_0=0.415cm, and an axial length l=20cm.

Located about 2mm past the exit ends 40 of the rods 38 is an exit lens 42. The lens 42 is simply a plate with an aperture 44 therein, allowing passage of ions through aperture 44 to a conventional detector 46 (which may for example be a channel electron multiplier of the kind conventionally used in mass spectrometers).

The rods 38 are connected to the main power supply 50 which applies a DC rod offset to all the rods 38 and also applies RF in conventional manner between the rods. The power supply 50 is also connected (by connections not shown) to the ion source 14, the aperture and orifice plates 18 and 24, the skimmer plate 32, and to the exit lens 42.

By way of example, for positive ions the ion source 14 may typically be at +5,000 volts, the aperture plate 18 may be at +1,000 volts, the orifice plate 24 may be at +250 volts, and the skimmer plate 32 may be at ground (zero volts). The DC offset applied to rods 38 may be -5 volts. The axis of the device, which is the path of ion travel, is indicated at 52.

Thus, ions of interest which are admitted into the device from ion source 14 move down a potential well and are allowed to enter the rods 38. Ions that are stable in the applied main RF field applied to the rods 38 travel the length of the device undergoing numerous momentum dissipating collisions with the background gas. However a trapping DC voltage, typically -2 volts DC, is applied to the exit lens 42. Normally the ion transmission efficiency between the skimmer 32 and the exit lens 42 is very high and may approach 100%. Ions that enter the main vacuum chamber 34 and travel to the exit lens 42 are thermalized due to the numerous collisions with the background gas and have little net velocity in the direction of axis 52. The ions also experience forces from the main RF field which confines them radially. Typically the RF voltage applied is

in the order of about 450 volts (unless it is scanned with mass) and is of a frequency of the order of about 816 kHz. No resolving DC field is applied to rods 38.

When a DC trapping field is created at the exit lens 42 by applying a DC offset voltage which is higher than that applied to the rods 38, the ions stable in the RF field applied to the rods 38 are effectively trapped.

However ions in region 54 in the vicinity of the exit lens 42 will experience fields that are not entirely quadrupolar, due to the nature of the termination of the main RF and DC fields near the exit lens. Such fields, commonly referred to as fringing fields, will tend to couple the radial and axial degrees of freedom of the trapped ions. This means that there will be axial and radial components of ion motion that are not mutually orthogonal. This is in contrast to the situation at the center of rod structure 38 further removed from the exit lens and fringing fields, where the axial and radial components of ion motion are not coupled or are minimally coupled.

Because of the fringing fields couple the radial and axial degrees of freedom of the trapped ions, ions may be scanned out of the ion trap constituted by rods 38, by the application to the exit lens 42 of a low voltage auxiliary AC field of appropriate frequency. (An example of the frequencies that may be used is given later in this description.) The auxiliary AC field may be provided by an auxiliary AC supply 56, which for illustrative purposes is shown as forming part of the main power supply 50.

The auxiliary AC field is an addition to the trapping DC voltage supplied to exit lens 42 and couples to both the radial and axial secular ion motions. The auxiliary AC field is found to excite the ions sufficiently that they surmount the axial DC potential barrier at the exit lens 42, so that they can leave axially in the direction of arrow 58. The deviations in the field in the vicinity of the exit lens 42 lead to the above described coupling of axial and radial ion motions enabling the axial

ejection at radial secular frequencies. This is in contrast to the situation existing in a conventional ion trap, where excitation of radial secular motion will generally lead to radial ejection and excitation of axial secular motion will generally lead to axial ejection, unlike the situation described above.

Therefore, ion ejection in a sequential mass dependent manner can be accomplished by scanning the frequency of the low voltage auxiliary AC field. When the frequency of the auxiliary AC field matches a radial secular frequency of an ion in the vicinity of the exit lens 42, the ion will absorb energy and will now be capable of traversing the potential barrier present on the exit lens due to the radial/axial motion coupling. When the ion exits axially, it will be detected by detector 46. After the ion is ejected, other ions upstream of the region 54 in the vicinity of the exit lens are energetically permitted to enter the region 54 and be excited by subsequent AC frequency scans.

Ion ejection by scanning the frequency of the auxiliary AC voltage applied to the exit lens is desirable because it does not empty the trapping volume of the entire elongated rod structure 38. In a conventional mass selective instability scan mode for rods 38, the RF voltage on the rods would be ramped and ions would be ejected from low to high masses along the entire length of the rods when the q value for each ion reaches a value of 0.907. After each mass selective instability scan, time is required to refill the trapping volume before another analysis can be performed. In contrast, when an auxiliary AC voltage is applied to the exit lens as described above, ion ejection will normally only happen in the vicinity of the exit lens because this is where the coupling of the axial and radial ion motions occurs and where the auxiliary AC voltage is applied. The upstream portion 60 of the rods serves to store other ions for subsequent analysis. The time required to refill the volume 54 in the vicinity of the exit lens with ions will always be shorter than the time required to refill the entire trapping volume. Therefore fewer ions will be wasted.

As an alternative, instead of scanning the auxiliary AC voltage applied to end lens 42, the auxiliary AC voltage on end lens 42 can be fixed and the main RF voltage applied to rods 38 can be scanned in amplitude, as will be described. While this does change the trapping conditions, a q of only about 0.2 to 0.3 is needed for axial ejection, while a q of about 0.8 to 0.907 is needed for radial ejection. Therefore, as will be explained, few if any ions are lost to radial ejection if the RF voltage is scanned through an appropriate amplitude range, except possibly for very low mass ions.

As a further alternative, and instead of scanning either the RF voltage applied to rods 38 or the auxiliary AC voltage applied to end lens 42, a further supplementary or auxiliary AC dipole voltage may be applied to rods 38 (as indicated by dotted connection 57 in Fig. 1) and scanned, to produce varying fringing fields which will eject ions axially in the manner described. As is well known, the dipole voltage is usually applied between an opposed pair of the rods 38, as indicated in Fig. 1a.

Alternatively, a combination of some or all of the above three approaches (namely scanning an auxiliary AC field applied to the end lens 42, scanning the RF voltage applied to the rod set 38 while applying a fixed auxiliary AC voltage to end lens 42, and applying an auxiliary AC voltage to the rod set 38 in addition to that on lens 42 and the RF on rods 38) can be used to eject ions axially and mass dependently past the DC potential barrier present at the end lens 42.

The device illustrated may be operated in a continuous fashion, in which ions entering the main RF containment field applied to rods 38 are transported by their own residual momentum toward the exit lens 42 and ultimate axial ejection. Thus, the ions which have reached the extraction volume in the vicinity of the exit lens have been preconditioned by their numerous collisions with background gas, eliminating the need for an explicit cooling time (and the attendant delay) as is required in most conventional ion traps. At the same time as ions are entering the region 60, ions are being ejected axially from region 54 in the

mass dependent manner described.

It is noted that the extraction volume 54 in the vicinity of the exit lens is quite small. The exit lens 42 is normally placed very close to the ends of the rods 38, e.g. 2mm from the rod ends (as mentioned). The penetration of the fringing fields from the exit lens 42 into the space between the rods 38 is believed to be very small, typically of the order of between 0.5mm and 1.0mm, so the extent of volume or region 54 is exaggerated in Fig. 1, for clarity of illustration.

As a further alternative, the DC offset applied to all four rods 38 (which in the example given is -5 volts) can be modulated at the same frequency as the AC which would have been applied to exit lens 42. In that case no AC is needed on exit lens 42 since modulating the DC offset is equivalent to applying an AC voltage to the exit lens, in that it creates an AC field in the fringing region. Of course the DC potential barrier is still applied to the exit lens 42. The amplitude of the modulation of the DC offset will be the same as the amplitude of the AC voltage which otherwise would have been applied to the exit lens 42, i.e. it is set to optimize the axially ejected ion signal. Then, either the RF amplitude is scanned to bring ions sequentially into resonance with the AC field created by the DC modulation, or else the frequency of the modulation is scanned so that again, when such frequency matches a radial secular frequency of an ion in the fringing fields in the vicinity of the exit lens, the ion will absorb energy and be ejected axially for detection. The rod offset would not be modulated until after ions have been injected and trapped within the rods, since the modulation would otherwise interfere with ion injection, so this process would be a batch process. This is in contrast to the continuous process possible when AC is placed on the exit lens, in which case ions can be ejected from the extraction region 54 at the same time as ions are entering region 60 (because the AC field on exit lens 42 does not affect ion injection).

The highest efficiency in a continuous mode operation is achieved when the ion ejection rate is faster than the rate at which ions of

the desired mass/charge ratio are injected into the rods and travel along them to the exit lens 42. Ion ejection processes can require some tens of milliseconds. The time required for ions to travel from one end to the other of the rods 38 depends on the lengths of the rods themselves, the initial energy of the ions, and the pressure in the vacuum chamber 34. In some cases the end-to-end transit time will dominate, but more often the time required to extract the ions from the region in the vicinity of the exit lens 42 will be more important. Thus it may be desirable to manipulate the axial energy of the ions to afford an optimum match between the time required for the ions to reach the extraction region 54, and the time for the ejection process itself to occur. Further, it may be of utility to be able to control the concentration of ions in the vicinity of the exit lens to reduce or enhance the local charge density in that region, depending on the application.

One method of matching the time required for ions to travel from one end to the other of the rods 38 to the time required to eject the ions is to apply an axial field along the rods 38. Methods for imposing axial fields of this kind are described in copending application serial no. 08/514,372 filed August 5, 1995 and entitled "Spectrometer with Axial Field" assigned to the assignee of this application. An applied axial field in the direction of the exit lens 42 will tend to concentrate ions in the region of rods 38 in the vicinity of lens 42, i.e. in the volume 54 of the device from which the ions are extracted. An applied axial field in the opposite direction will tend to deplete ions from the extraction volume 54, and may also be desirable in some cases.

Several techniques are available as described in the above identified copending application serial no. 08/514,372 for providing an axial field by modification of the electrode geometries. Such arrangements include tapering the rods, or locating one pair of rods nearer the center line at one end of the device and the other pair of rods nearer the center line at the other end of the device, or segmenting the rods axially and applying different DC offsets to successive segments. The disclosure and

drawings of said application are hereby incorporated by reference into this application.

One typical electrode geometry which may be used is that depicted in Fig. 2, where primed reference numerals indicate parts corresponding to those of Fig. 1. Here, the rods 38' are divided into segments 38-1' to 38-5', with DC offsets V1 to V6 which increase in negative value applied to successive segments from 38-1' to 38-6'. This arrangement will provide an axial field as described in said application. Such an arrangement will strongly concentrate ions in the volume near the exit lens 42' and will increase the coupling of axial and radial ion motion.

If desired, the axial field can be oscillated as described in the above mentioned copending application. Such oscillation may enhance axial ejection of ions trapped in the volume near the exit lens 42. It can also be used for ion dissociation as described in said application, by oscillating the ion population trapped in the rod structure about their equilibrium positions.

The system described can be considered as being an open-ended three-dimensional ion trap, where the open end is an integrated high efficiency ion injection device (supplied by ion source 14). The ions in the vicinity of the exit lens 42 experience a three-dimensional trapping field comprised of radial and axial components. Radially the ions are contained by the main RF field applied to the linear rods 38. Axially the ions are contained at the exit end of the device by the DC potential on the exit lens 42, and are contained at the entrance end of the device by the potential gradient from the applied axial field (or from the skimmer 32). The ions are also to some extent contained in the trapping region or volume 54 by the field created by the build-up of charge density upstream of that region. It will therefore be appreciated that the actual trapping volume 54 is variable along the axial or Z direction.

If desired, the RF on the rods 38 can be scanned to eject ions mass dependently, while keeping a DC potential barrier on end lens 42 but with no AC field on end lens 42, no modulation of the DC offset on rods

38, and no dipole AC field on rods 38. In that case, ions in the fringing fields at the downstream ends of rods 38 will leave axially and be detected, but most of the ions between rods 38 (those in region 60) will leave radially and will be wasted. The wastage can be reduced by segmenting rods 38 as shown in Fig. 2, making the last set of segments 38-5' very short (e.g. less than 1cm), and scanning the RF for ejection only on segments 38-5'. In this way, a higher proportion of the ions between rods 38-5' will be ejected axially mass dependently, for detection.

Often many of the ions from conventional ion sources are of little or no analytical utility. Examples of such ions are low mass solvent and cluster ions. These ions simply serve to increase the overall charge density within the ion trap at the expense of optimum performance. Various techniques may be used to eliminate such unwanted ions from the linear ion trap described. One such method is to operate the main RF voltage from power supply 50 at a level where the analytes of interest are stable within the rod structure 38, but the unwanted ions are unstable. For example if the unwanted ions are in the mass to charge range 10 to 100, and the ions of interest are in the mass to charge range 200 to 1,000, then the main RF voltage can be operated at 214 volts peak to peak.

Another method of eliminating unwanted ions from the ion trap is to apply an additional auxiliary AC voltage between opposite pairs of the rods 38, to resonantly eject the unwanted ions radially out of the rod set. This technique is well known, as mentioned. In the technique an auxiliary AC voltage, of magnitude equal to about 10% of the level of the main RF voltage and of much lower frequency, is typically applied between opposite pairs of rods. The auxiliary AC voltage, of appropriate amplitude and frequency, may be scanned to resonantly eject unwanted ions radially.

The use of resonant ejection to eject ions is disclosed in Langmuir U.S. patent 3,334,225, in Syka et al. U.S. patent Re34,000, and in Kelley U.S. patent 5,381,007 and is also disclosed in Douglas U.S. patent 5,179,278 assigned to the assignee of this application.

Another technique for removing unwanted ions is to apply low voltage DC to opposite pairs of rods to make the rods 38 act as a low resolution mass spectrometer. The magnitude of the DC applied will be such that the combination of AC and DC ejects ions only in the low mass range which is not of interest.

Finally, unwanted ions can be eliminated from rods 38 by the application of a filtered noise field to the rods, such that only ions of interest are stable within the rod structure and can be stored. The use of such a filtered noise field is disclosed in Langmuir U.S. patent 3,334,225 issued August 1, 1967 and in Kelley U.S. patent 5,381,007 issued January 10, 1995.

One of the disadvantages of most ion traps is that as mentioned, they cannot accept additional ions while performing an analysis. When using continuous ion sources this leads to reduced duty cycles and decrease overall sensitivity, since many or in fact most of the ions generated by the source are not analyzed and are wasted. Douglas U.S. patent 5,179,278 teaches that a multipole inlet system can reduce these problems by accepting and storing ions from the ion source while the ion trap is performing an analysis. This can dramatically enhance the overall system sensitivity by increasing duty cycle. Figure 3 illustrates a device which uses these principles.

In the Fig. 3 device, in which double primed reference numerals indicate parts corresponding to those of Fig. 1, the rods 38" have been divided into three sets of rods 38a, 38b and 38c. Rods 38a are used to pre-trap ions from the continuous ion source 14". The rods 38b are used as an RF rod mirror that can reflect or transmit ions, by changing the DC offset of rods 38b. The rods 38c and lens 42" serve as the open-ended ion trap previously described, for analysis of ions which are injected into rods 38c through the rods 38b.

In operation, the RF and DC voltages on rod set 38a are set to accept ions within a mass range of interest, while the AC and DC voltages on rod set 38b are set to reflect ions, so that a population of ions

accumulates in rod set 38a. (The operation is exactly as described for rod set 44 in U.S. patent 5,179,278.) After a predetermined time, the voltages on rod set 38b are changed to allow passage of the accumulated ions in rod set 38a through rod set 38b to rod set 38c. The RF voltage and DC offset voltage applied to rod set 38c, and the AC and DC voltages applied to lens 42", are set such that rod set 38c operates as an ion trap with axial ejection as described in connection with Fig. 1. Thus, ions are axially ejected in a mass dependent manner from rod set 38c, as previously described, for detection in detector 46".

While mass analysis is being performed in rod set 38c, the voltages on rod set 38b return to the ion reflection mode and further ions from the source 14" are stored in rod set 38a. An advantage of this configuration is that while ions are being analyzed in rod set 38c, ions from the continuous source are accumulated for subsequent analysis in the pre-trapping region, i.e. rod set 38a, and are not lost. As U.S. patent 5,179,278 teaches, proper optimization of the time to collect sufficient ions to fill the analysis region of the device, the time to empty the pre-trap region, and the time to perform analysis can result in very high duty cycles, and thus high overall sensitivity. Of course even in the Fig. 1 arrangement, ions are collected in region 60 of rods 38 while ions from the extraction region 54 are being ejected, so that some ions can be collected while the ion trap constituted by rods 38 and lens 42 is scanning out ions. However the Fig. 3 version allows storage of more ions since a larger volume can be used. In addition, some DC can conveniently be applied between the pairs of rods of rod set 38a to eliminate unwanted ions, thus reducing space charge effects in rod set 38c.

By way of example, 0.1µM (micro moles) of reserpine (having mass to charge ratio 609) was introduced using the well known ion spray source (not shown) into a conventional mass spectrometer model API 300 produced by Sciex Division of MDS Health Group Limited of Concord, Ontario, Canada. A simplified diagrammatic view of the model API 300 ion optical path is shown in Fig. 4, where the gas curtain entrance plate is

indicated at 70, the gas curtain exit plate is indicated at 72, the skimmer plate is shown at 74, and four sets of rods are indicated as Q0, Q1, Q2 and Q3, with orifice plates IQ1 between rod sets Q0 and Q1, IQ2 between Q2 and Q3, and IQ3 between Q2 and Q3. The exit lens is indicated at 76 and the detector (a channel electron multiplier) is indicated at 78.

In the Fig. 4 example, the pressures were 2.2 Torr in chamber 80, 8 milli-Torr in chamber 82 and 2 x 10^{-5} Torr in the remainder of the vacuum chamber 84. The applied DC voltages were: ground at skimmer plate 80; -5 volts DC at Q0, -7 volts DC at IQ1, -10 volts at Q1, -20 volts at IQ2, -7 volts DC at Q2, -3 volts DC at IQ3 (which served as the equivalent of the exit lens 42); -15 volts DC on Q3, and 0 volts on the final exit plate 76. All resolving DC voltages were removed from the quadrupoles.

Q2, which was normally a collision cell, was configured to trap ions and had a cell pressure of 1 x 10^{-3} Torr. In addition, an auxiliary AC voltage was applied to the exit lens IQ3. The auxiliary AC power supply could produce 100 volts peak to peak, at frequency one-ninth that of the main RF frequency, and was phase locked to the main RF frequency. (The main RF frequency was 816 kHz so that of the auxiliary AC voltage was 91.67 kHz.)

The auxiliary AC voltage was held at 47 volts peak to peak, its frequency was held constant at 91.67 kHz for the experiment, and the RF voltage applied to the Q2 rods was scanned to obtain a mass spectrum. Although scanning the amplitude of RF voltage changes the trapping conditions and could eject very low mass ions, the q of the device is so low under the conditions described that ions of interest trapped in the rod set Q2 are not normally ejected (unless the experimenter is interested in extremely low mass ions).

The sequence of events in the experiment was:

(a) A short pulse of ions was allowed to pass from Q0 into Q2 (Q1 performed no function except as an ion pipe during this experiment) by changing the DC lens voltage on IQ1 from +20 volts (which stopped ions) to -

7 volts (for ion transmission).

(b) Ions that were trapped in Q2 were then scanned out axially by ramping the RF applied to the Q2 rods, typically from 924 volts peak to peak to 960 volts peak to peak.

(c) Q2 was then emptied of any residual ions by reducing the RF applied to its rods to a very low voltage, typically 20 volts peak to peak.

(d) The sequence was then repeated.

A typical spectrum produced using this technique is shown in Fig. 5, which shows a peak 100 at mass 529.929. Since the spectrum was not mass calibrated, the reported peak of 529.929 was incorrect; the true mass was 609.

It will be seen that the peak width at half height, corrected manually for the mass calibration offset, is 0.42 AMU. This yields an $M/\Delta M$ resolution value at M/Z609 of about 1450, which is a very high resolution. In the example shown, good resolution was best obtained by scanning slowly, at a scan speed in this example of 78 AMU per second. However with optimization, higher scan rates are expected to be achieved.

In another experiment performed with the Fig. 4 apparatus, fragmentation was performed under the following conditions:

(a) Two volts trapping DC were applied to lens IQ3.

(b) 62 volts (peak to peak) AC at 91.67 kHz were applied to lens IQ3.

(c) Q1 was set to a resolving mode (RF and DC were applied) to allow only transmission of a selected parent ion, namely renin substrate tetra decapeptide $(M + 3H)^{3+}$ at m/z 587.

(d) Q3 was set to RF only (the resolving DC was removed).

(e) Q2 was pressurized with 1×10^{-3} Torr helium.

The experimental steps were:

1. A pulse of m/z 587 ions was allowed to pass from Q0 to

Q2 by changing the voltage on lens IQ1 from 20 volts to -7 volts.

2. Ions within Q2 were excited by setting the RF rod voltage to 897.8 volts peak to peak for 50 ms. This was an excitation step. Ions in Q2 which were in resonance with the applied AC field (on IQ3) were excited (absorbed power) and, because of their increased kinetic energy, were either ejected from the trap or fragmented due to collisions with the background gas.

3. Immediately after the 50 ms excitation step, ions in Q2 were scanned out axially by scanning the Q2 RF rod voltage from 800 volts peak to peak to 1,422 volts peak to peak. This step simply took a "snapshot" of the ions that had remained in the trap after the excitation step.

The observed ions are shown at peaks 104, 106, 108 in Fig. 6. Again the mass spectrum was not calibrated and is shown corrected. Peak 108 is the parent ion at m/z 587 (triply charged), while the fragment ions m/z 697 and m/z 720 are shown at 106, 108 (they have higher m/z ratios because they are only doubly charged).

Thus, it will be seen that collisional fragmentation can readily be performed in the linear trap described, and the fragment ions can be scanned axially in a mass dependent manner for detection and analysis.

While the invention has been described in connection with a quadrupole rod structure, other multipole rod geometries may be used, for example octopoles and hexapoles. In addition, although the exit lens 42 has been described as a plate with an aperture, other configurations of exit lenses may be used, for example a short RF-only rod array such as that indicated at 102 in Fig. 7 and having A and B poles 102a, 102b. The rod offsets of the A and B poles 102a, 102b may then be resonated at the resonance frequency of the ion to be ejected, producing axial ejection as was achieved by the auxiliary AC field applied to exit lens 42.

While linear rod sets have been described and illustrated, if

desired curved rod sets may be used. In addition, while end lenses in the form of a perforated plate, or a short set of rods, have been shown, other forms of end lenses may be used. For example, as shown in Fig. 8, the end lens 110 may be a segmented plate having wedge-shaped segments 110-1, 110-2, 110-3, 110-4 and an aperture 112. This allows different fields to be applied to each segment, to optimize the results, while still limiting the quantity of gas which can leave the part of the vacuum chamber upstream of lens 110.

While preferred embodiments of the invention have been described, it will be appreciated that various changes may be made within the scope of the invention, and all such changes are intended to be included in the accompanying claims.

CLAIMS:

1. A method of operating a mass spectrometer having an elongated rod set, said rod set having an entrance end and an exit end and a longitudinal axis, said method comprising:

(a) admitting ions into said entrance end of said rod set,

(b) trapping at least some of said ions in said rod set by producing a barrier field at an exit lens adjacent to the exit end of said rod set and by producing an RF field between the rods of said rod set adjacent at least the exit end of said rod set,

(c) said RF and barrier fields interacting in an extraction region adjacent to said exit end of said rod set to produce a fringing field,

(d) energizing ions in said extraction region to mass selectively eject at least some ions of a selected mass to charge ratio axially from said rod set past said barrier field,

(e) and detecting at least some of the axially ejected ions.

2. A method according to claim 1 wherein said barrier field is a DC field.

3. A method according to claim 2 wherein an auxiliary AC voltage is applied to said exit lens.

4. A method according to claim 3 wherein, in said step (d), said auxiliary AC voltage is scanned.

5. A method according to claim 1 or 2 wherein a DC offset voltage is applied to said rods, and in said step (d), said DC offset voltage is

modulated at a frequency to excite selected ions whereby selected ions are mass dependently ejected axially past said barrier field.

6. A method according to claim 1, 2 or 3 wherein, in said step (d), said RF field is scanned.

7. A method according to claim 1, 2 or 3 wherein, in said step (d), the amplitude of said RF field is scanned.

8. A method according to claim 1, 2 or 3 wherein, in said step (d), a supplementary AC voltage is applied between the rods of said rod set.

9. A method according to claim 1, 2 or 3 wherein, in said step (d), a supplementary AC voltage is applied between the rods of said rod set and said supplementary AC voltage is scanned.

10. A method according to claim 3 or 4 wherein said auxiliary AC voltage has a frequency which is synchronized and phase locked to the frequency and phase of said RF field.

11. A method according to claim 1, 2 or 3 and including the step of applying an axial field along said axis of said rod set.

12. A method according to claim 1, 2 or 3 and including the step of providing a low pressure gas between the rods of said rod set for collisional focussing and cooling of ions therein.

13. A method according to claim 1, 2 or 3 and including the step of providing said ions from an ion source, providing a second rod set between said first mentioned rod set and said ion source, pre-trapping ions in said second rod set, and selectively admitting ions from said second rod set into said first mentioned rod set for axial ejection from said first

mentioned rod set and consequent detection.

14. A method according to claim 1, 2 or 3 and including the step of ejecting radially from said rod set at least some ions outside a selected mass range of interest, before said step of axially ejecting ions.

15. A method according to claim 1 and including the step, before axially ejecting said ions, of exciting said ions to dissociate at least some of said ions.

16. A method according to claim 15 wherein said ions are excited by applying an axial field to said ions and oscillating said axial field.

17. A method according to claim 1, 2 or 3 wherein, at the same time as ions are being admitted into said entrance end of said rod set, ions are being mass selectively ejected axially from said exit end of said rod set, past said barrier field.

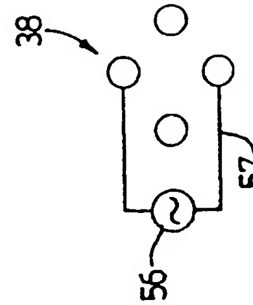
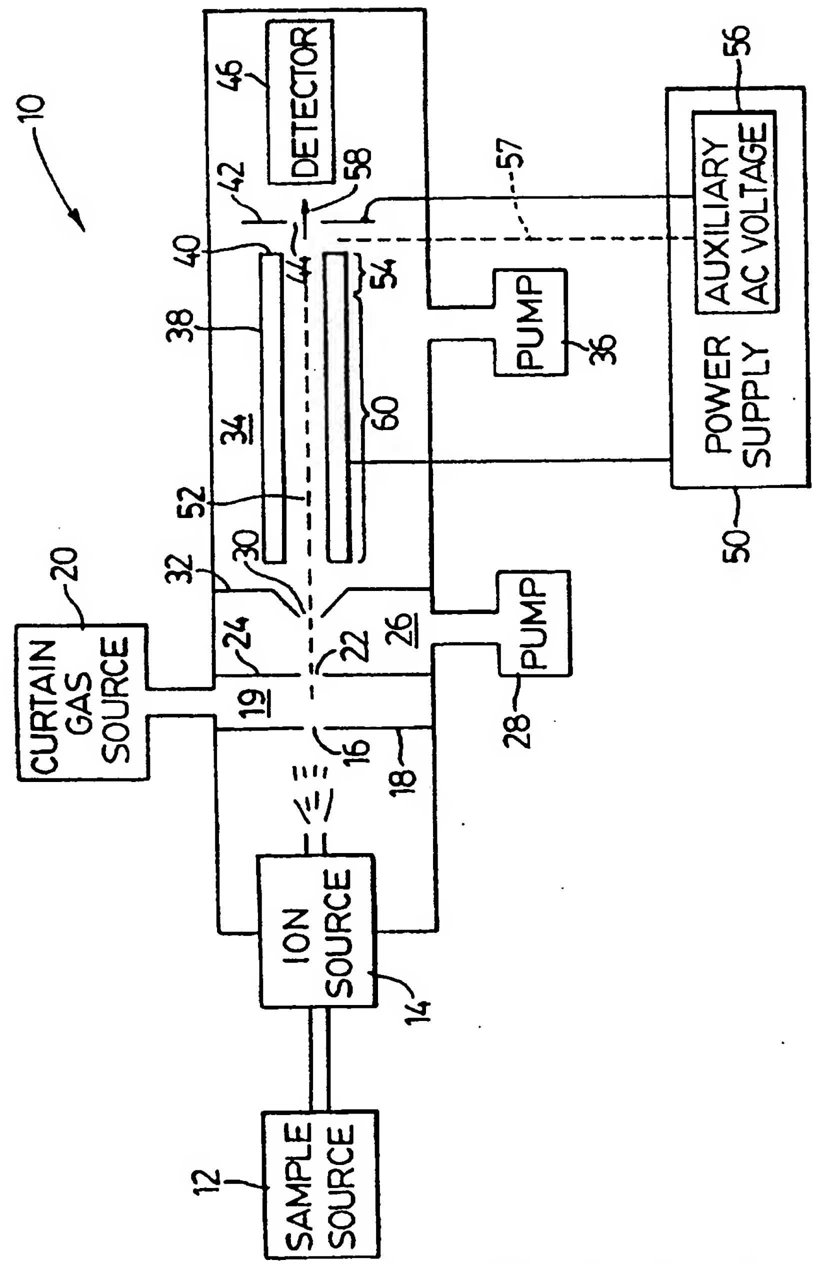

38
56
57

FIG. 1a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12
ION SOURCE
14
CURTAIN GAS SOURCE
20
16
18
19
24
22
26
28
PUMP
30
32
52
34
38
40
42
44
58
54
60
46
DETECTOR
PUMP
36
57
POWER SUPPLY
50
AUXILIARY AC VOLTAGE
56

FIG. 1

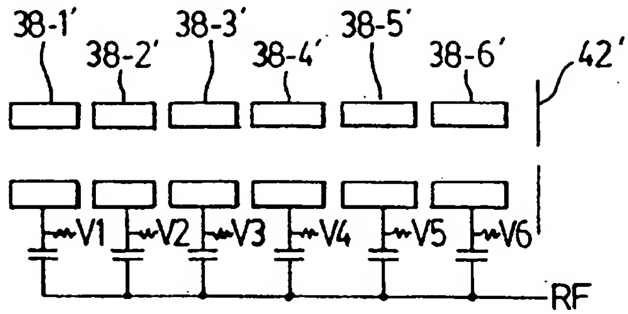


FIG. 2

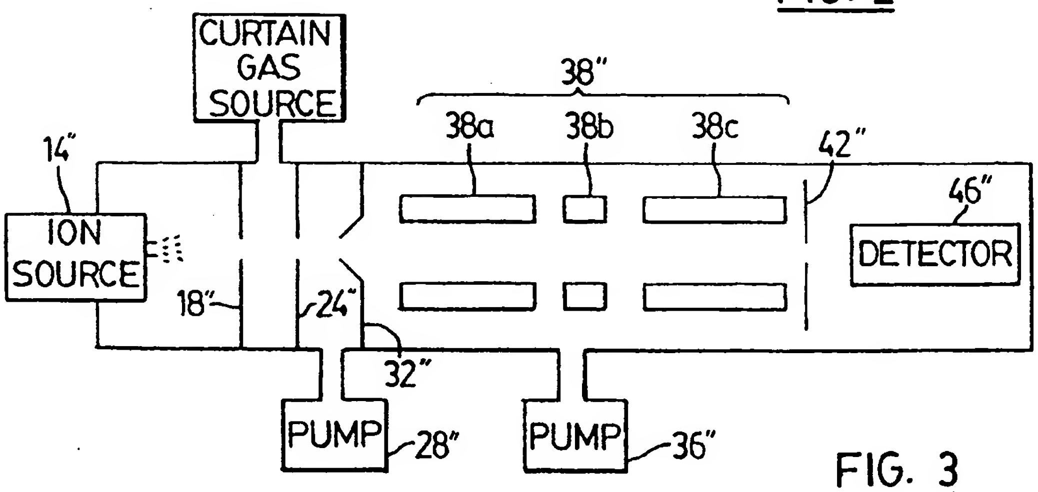


FIG. 3

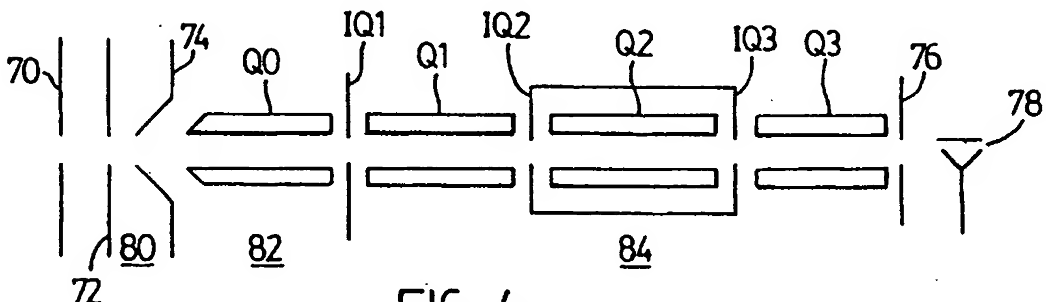
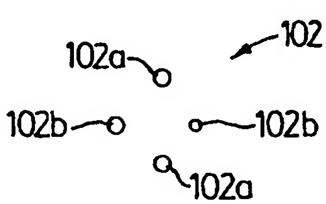


FIG. 4



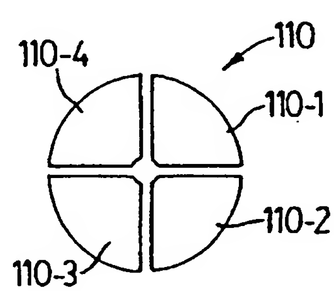


FIG. 7

FIG. 8

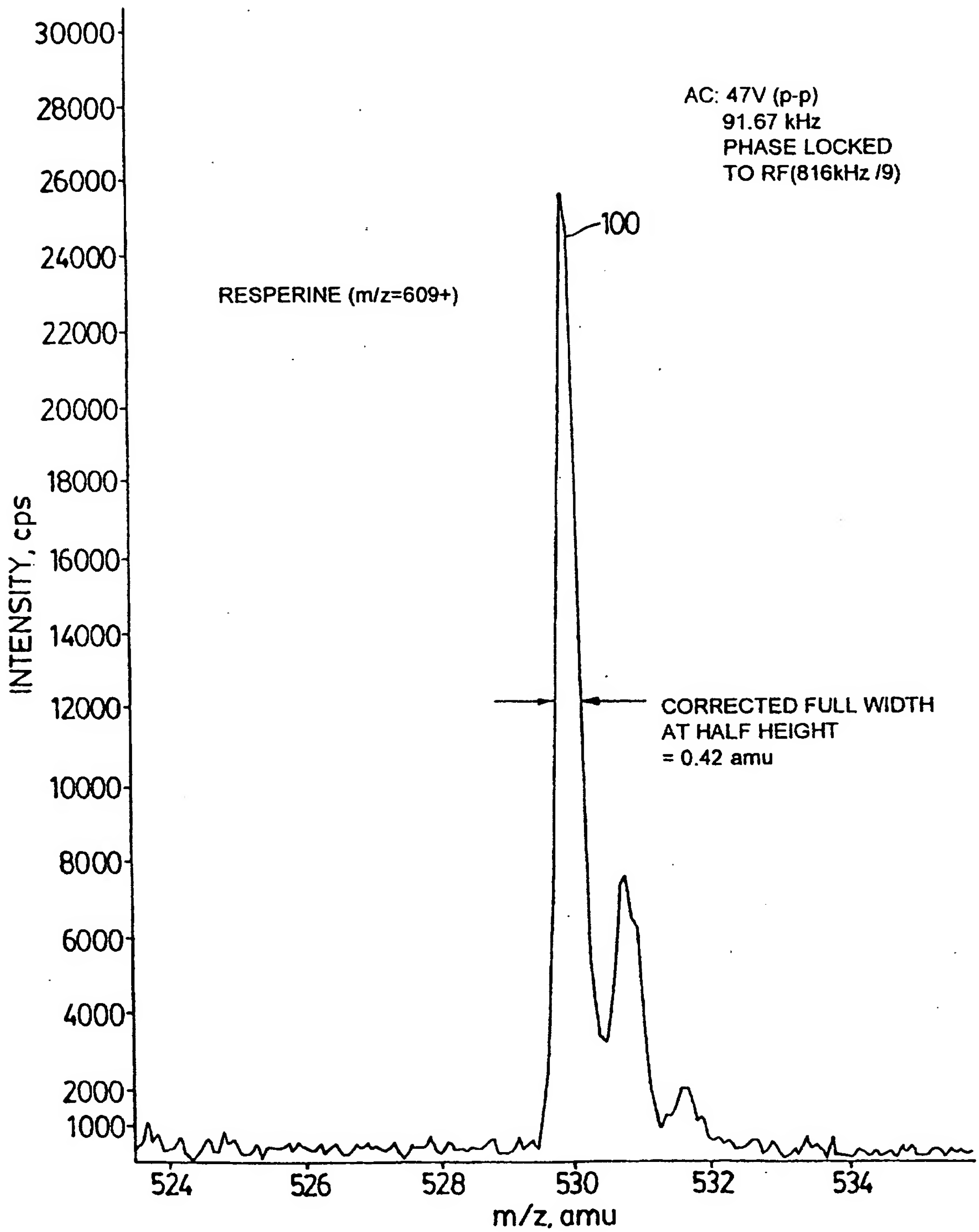

30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
1000
INTENSITY, cps
AC: 47V (p-p)
91.67 kHz
PHASE LOCKED
TO RF(816kHz /9)
100
RESPERINE (m/z=609+)
CORRECTED FULL WIDTH
AT HALF HEIGHT
= 0.42 amu
524
526
528
530
532
534
m/z, amu

FIG. 5

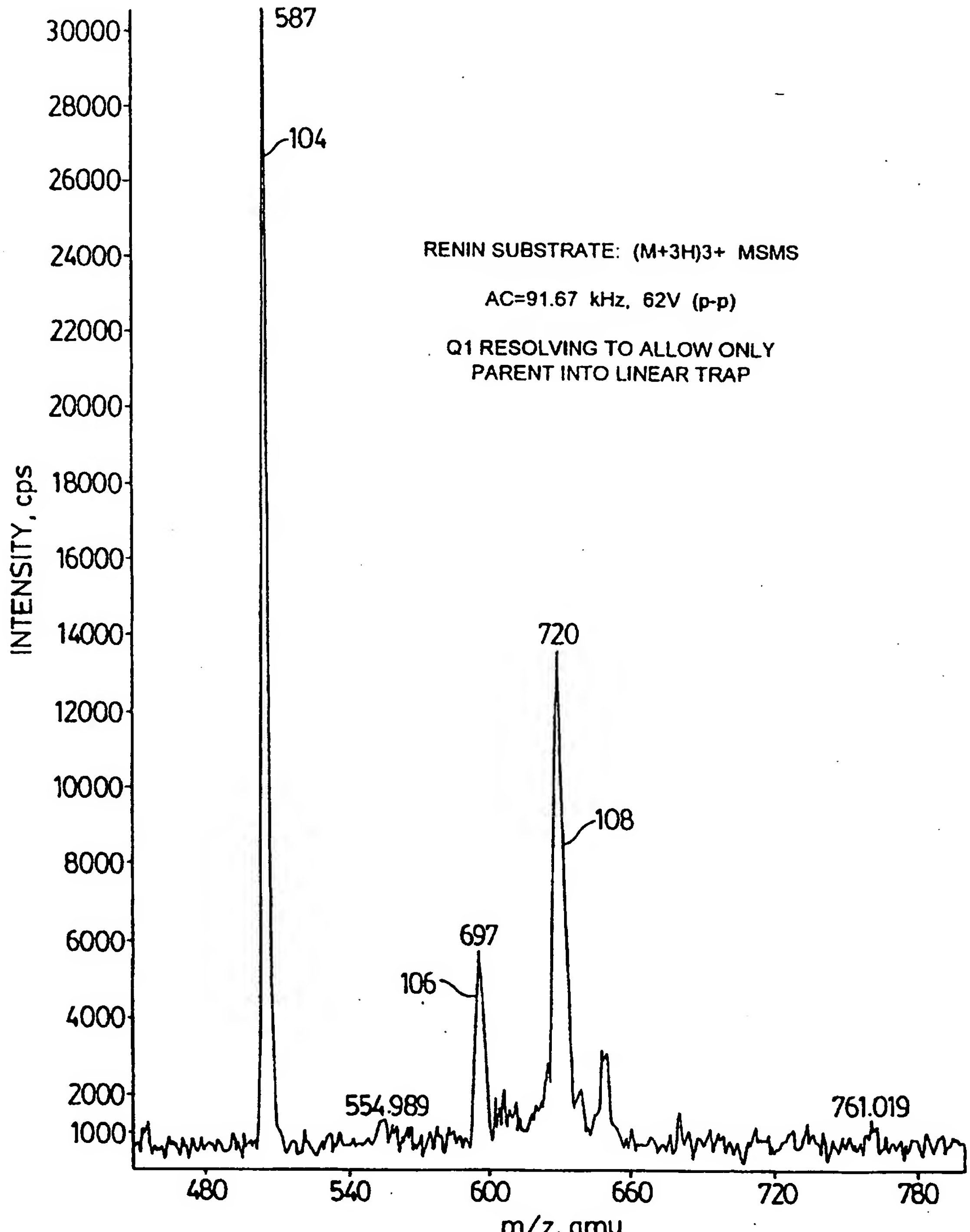

587
104
RENIN SUBSTRATE: (M+3H)3+ MSMS
AC=91.67 kHz, 62V (p-p)
Q1 RESOLVING TO ALLOW ONLY
PARENT INTO LINEAR TRAP
720
108
697
106
554.989
761.019
INTENSITY, cps
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
1000
480
540
600
660
720
780
m/z, amu

FIG. 6

ERNATIONAL SEARCH REPORT

Internat Application No
PCT/CA 97/00381

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 H01J49/42

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 H01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	EP 0 738 000 A (BRUKER FRANZEN ANALYTIK GMBH) 16 October 1996 see column 9, last paragraph; claims 1,4,5,9,13,14; figure 1 ---	1
A	US 5 206 506 A (N. J. KIRCHNER) 27 April 1993 see column 29, line 5 - line 31; claim 26 ---	1
A	EP 0 529 885 A (MDS HEALTH GROUP LTD) 3 March 1993 cited in the application see abstract see page 4, last paragraph; figure 1 ---	1

-/--

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

1

Date of the actual completion of the international search	Date of mailing of the international search report
27 August 1997	03.09.97

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Hulne, S

Form PCT/ISA/210 (second sheet) (July 1992)

International Application No
PCT/CA 97/00381

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 420 425 A (BIER MARK E ET AL) 30 May 1995 cited in the application see column 13, last paragraph - column 15, paragraph 1; figures 7A,7B,7C -----	1

1

TERNATIONAL SEARCH REPORT

Ii. nation on patent family members

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PCT/CA 97/00381

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